
Preliminary Atom-Probe Tomographic (APT) Analyses of Nb Cavity Materials

Dr. Jason Sebastian

Prof. David Seidman

Northwestern University Department of Materials Science and Engineering

Cook Hall, 2220 North Campus Drive, Evanston, IL 60208

Northwestern University Center for Atom-Probe Tomography (NUCAPT)

<http://arc.nucapt.northwestern.edu>

Dr. Jim Norem

High Energy Physics Division, Argonne National Laboratory (ANL), Argonne, IL 60439

Dr. Pierre Bauer

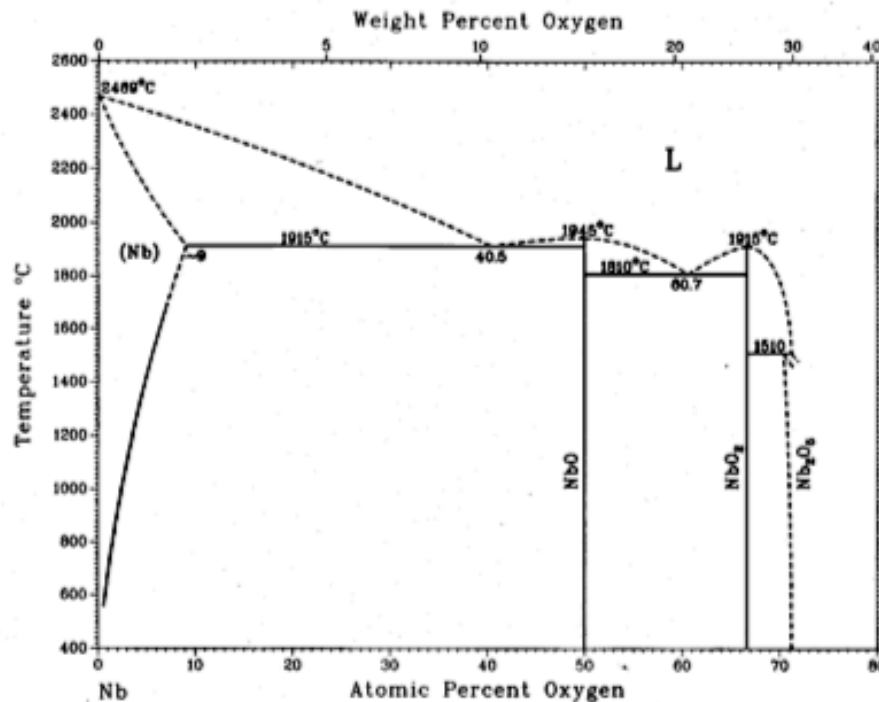
Technical Division, Fermi National Accelerator Laboratory (FNAL), Batavia, IL 60510

Agenda

- Background
 - Superconducting Nb rf cavities
 - Atom-Probe Tomography (APT)
- Specimen preparation
- Preliminary APT results
 - Three analyses (separate tips)
- Conclusions and next steps

The Nb-O phase diagram - a variety of different oxide phases can form

- NbO, NbO₂, and Nb₂O₅ are the thermodynamic equilibrium phases
- Other phases (e.g., Nb₂O₃ and Nb₂O) also reported
- Kinetic effects must also be considered



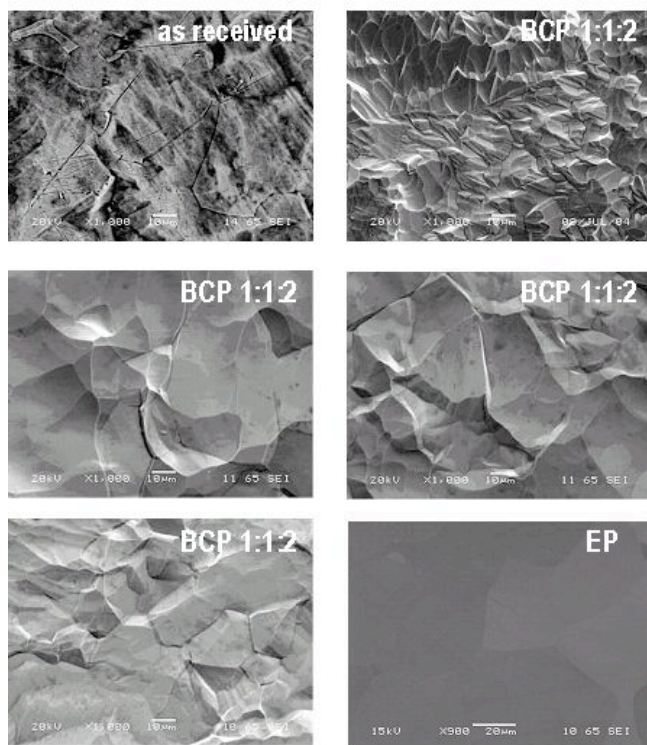
From Binary Alloy Phase Diagrams (2nd Ed.), ASM (1990)

Phase	Composition (at. % O)	Pearson symbol	Space group	Prototype
(Nb)	0 to ~9	cI2(bar)	Im3(bar)m	W
NbO	50	cP6	Pm3(bar)m	NbO
NbO ₂	66.7	tI96	I41/a	
Nb ₂ O ₅	~71.4	mP99	P2/m	

Studies of Nb cavity materials

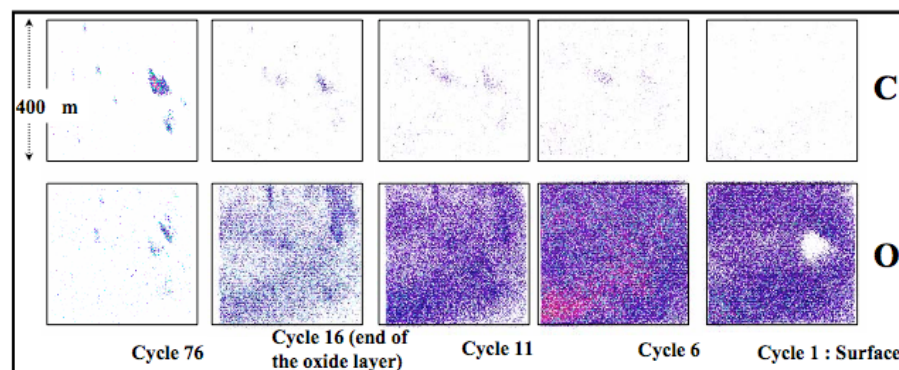
- SEM micrographs from P. Bauer (et al.)

Surfaces:

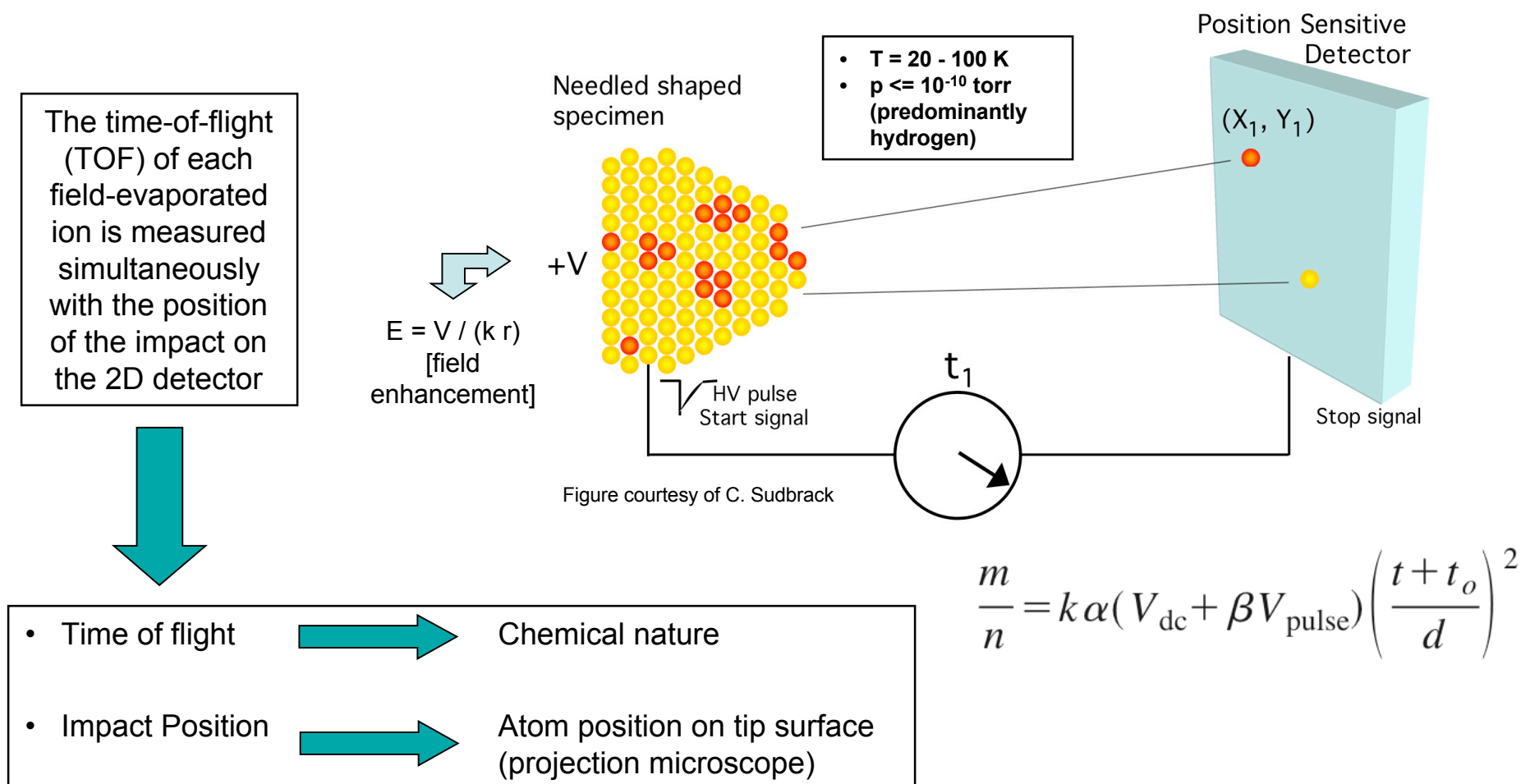


C. Chapman, D. Hicks, C. Boffo

- SIMS studies by C. Antoine

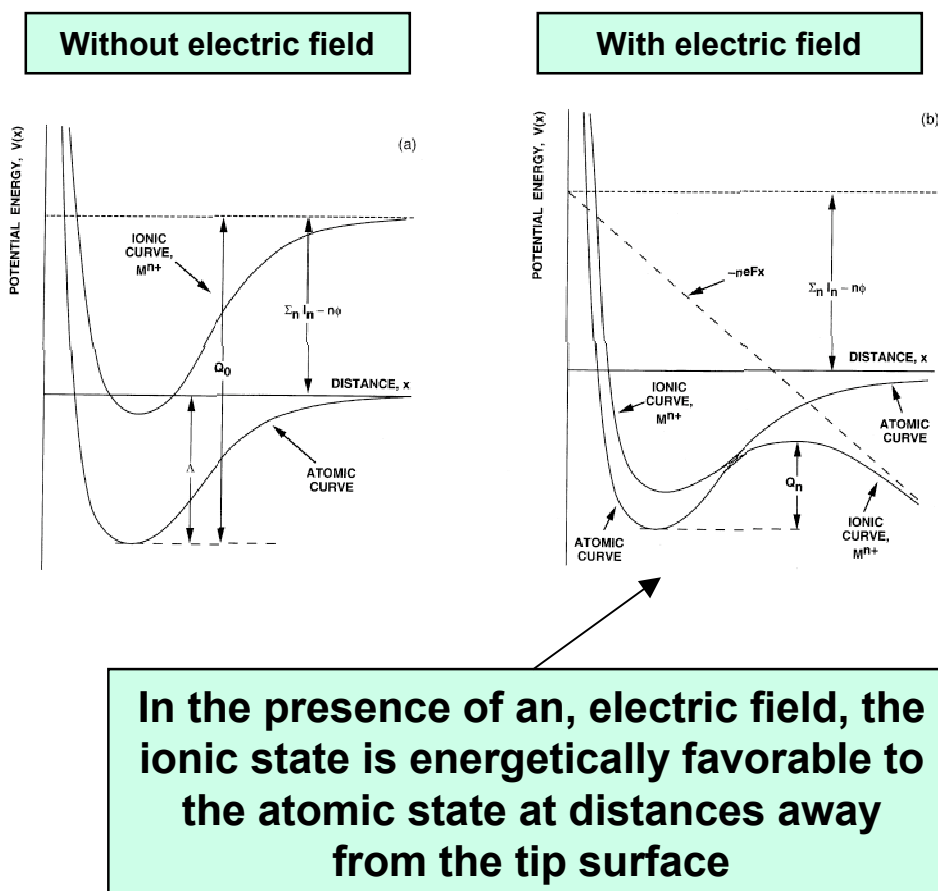


Atom-probe tomography (APT) - schematic



Field evaporation - schematic

- A thermally-activated process involving the excitation of a surface atom over a Schottky hump in the presence of an electric field
 - In an atom probe, evaporation is controlled via the use of a high-voltage pulser, or high frequency (femtosecond) pulsing laser



From Miller et al., (1996)

NUCAPT's new local electrode atom-probe (LEAP) tomograph takes atom-probe microscopy to a new level

- **Increased data collection rate (up to 72 million ions hr^{-1})**
- **Expanded specimen geometry capabilities**
- **Analysis volumes of, for example, 50 nm x 50 nm x 400 nm (= 1,000,000 nm³ = 0.001 μm^3)**

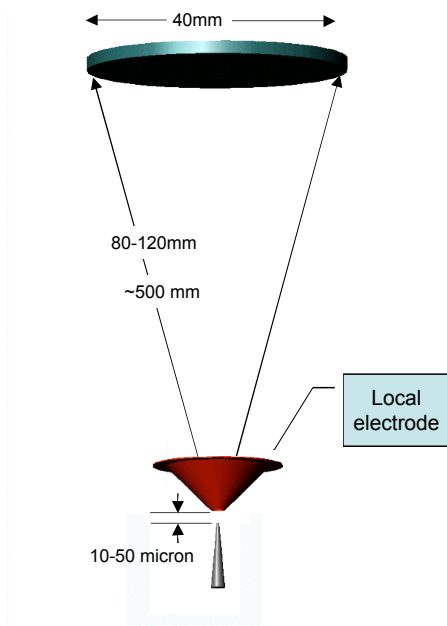
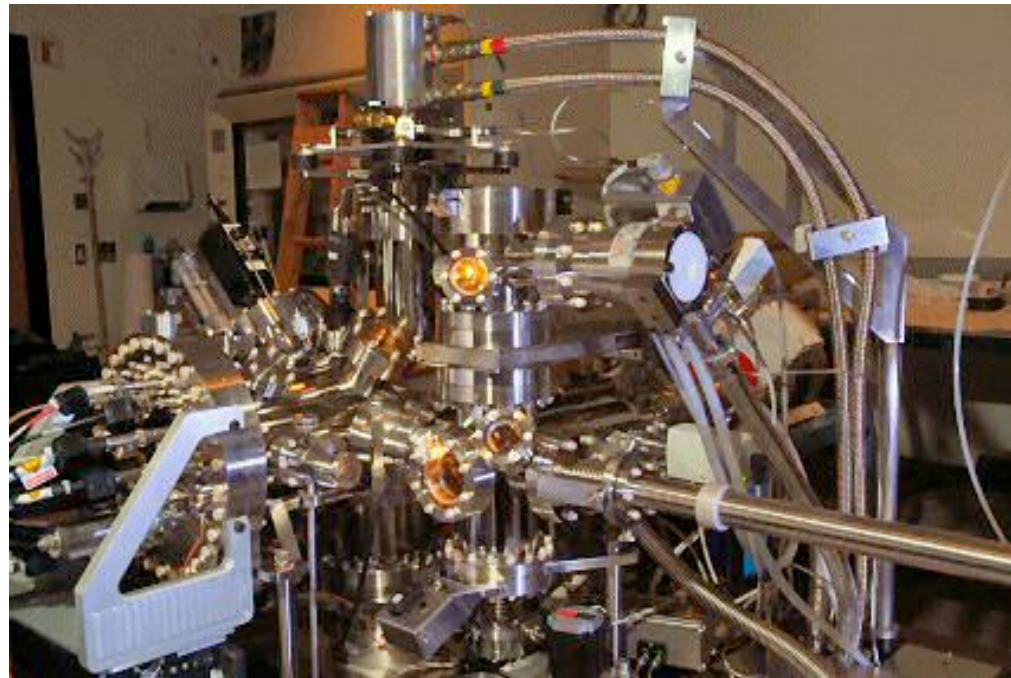


Figure courtesy of Imago Scientific Instruments



NUCAPT's LEAP Tomograph

Specimen preparation

1. Electropolishing

- 10% HF (48%) in 90% HNO₃ (68%)
- DC voltage
- “Drop off” technique
- Keep things as clean as possible
 - Rinsing (UHP water)
 - Minimal time in air (stored in desiccator under dry N₂)

2. Buffered Chemical Polishing (BCP)

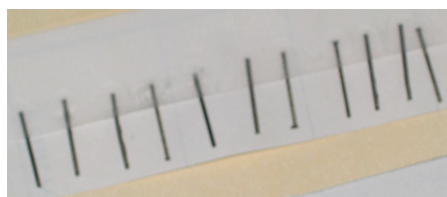
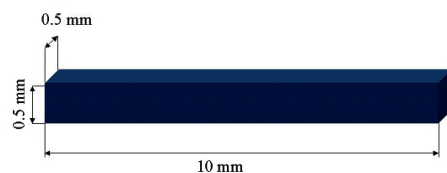
- 1 : 1 : 2
HF (49%) : HNO₃ (68%) : H₃PO₄ (85%)
- No voltage
- Replicating the setup at FNAL

3. Focused ion beam (FIB) milling at ANL to be done soon

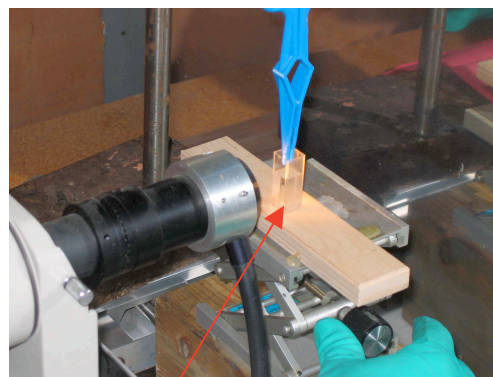
- “Site-specific” specimen preparation

Specimen preparation - electropolishing and buffered chemical polishing

Step 1 - Machining Blanks (EMD machined at FNAL from Nb cavity material)



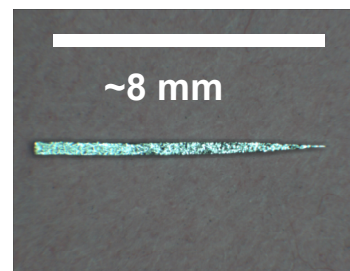
Step 2 - Polishing at FNAL



Rectangular
cuvette with
polishing
solution (BCP)

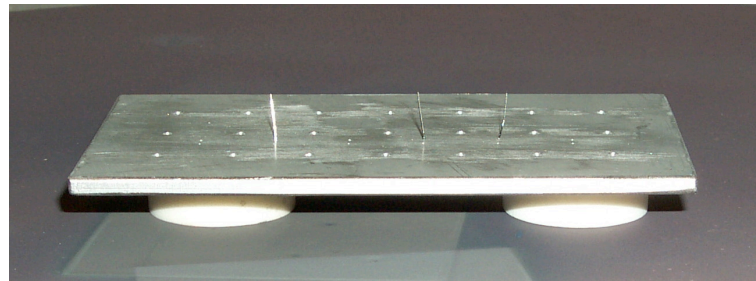


Stereo-
microscope

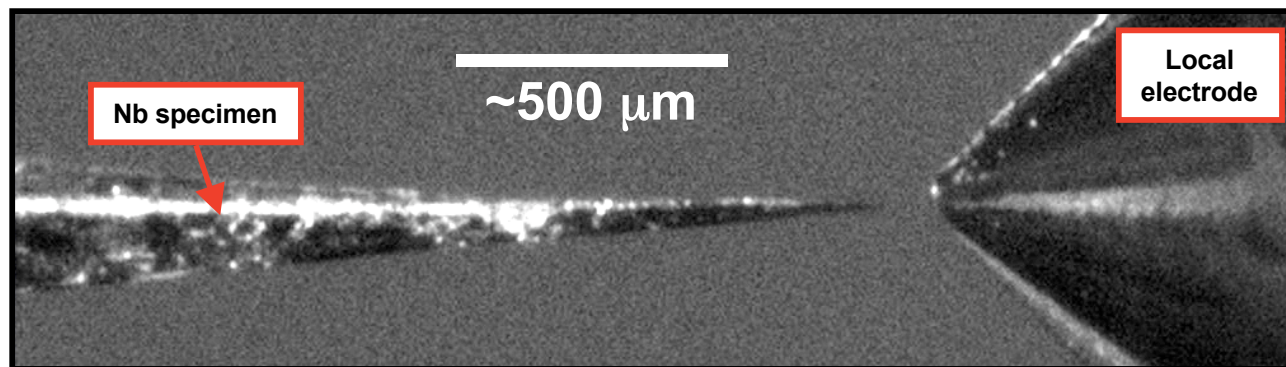


Specimen preparation - electropolishing and buffered chemical polishing

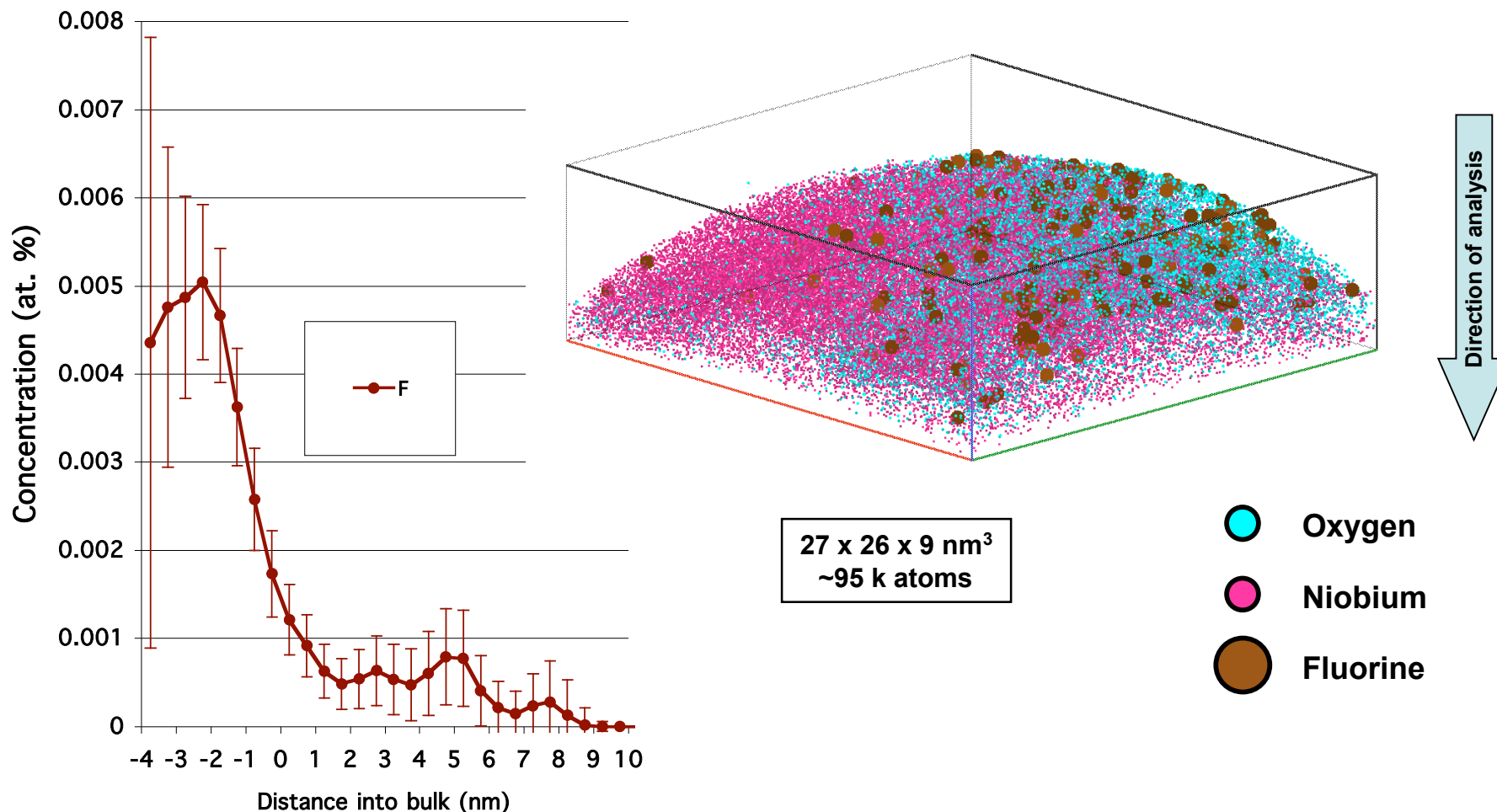
Step 3 - Heat treatment at FNAL



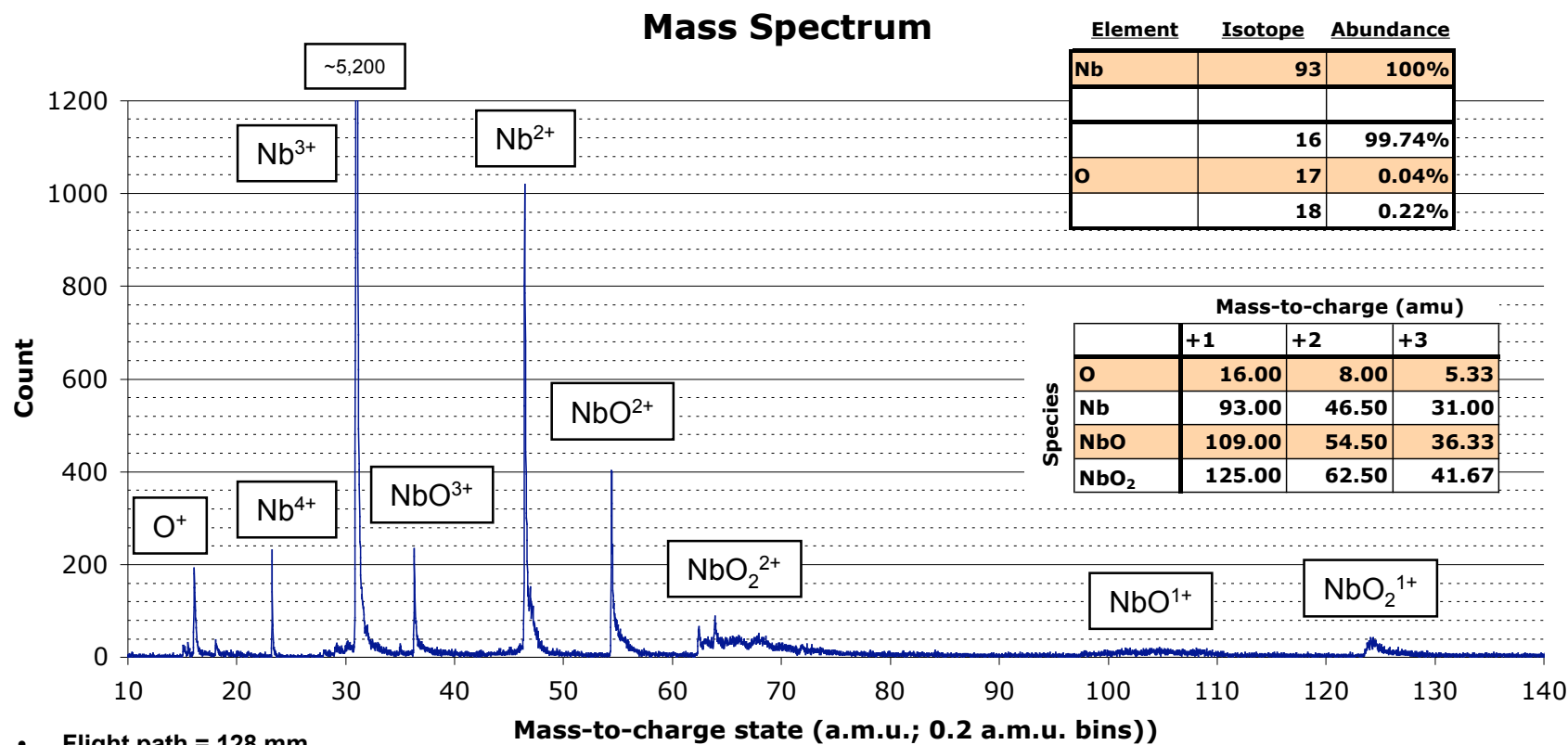
Step 4 - Alignment in the LEAP



Atomic sensitivity of the technique - individual fluorine atoms on and near the surface (propensity for the oxide)

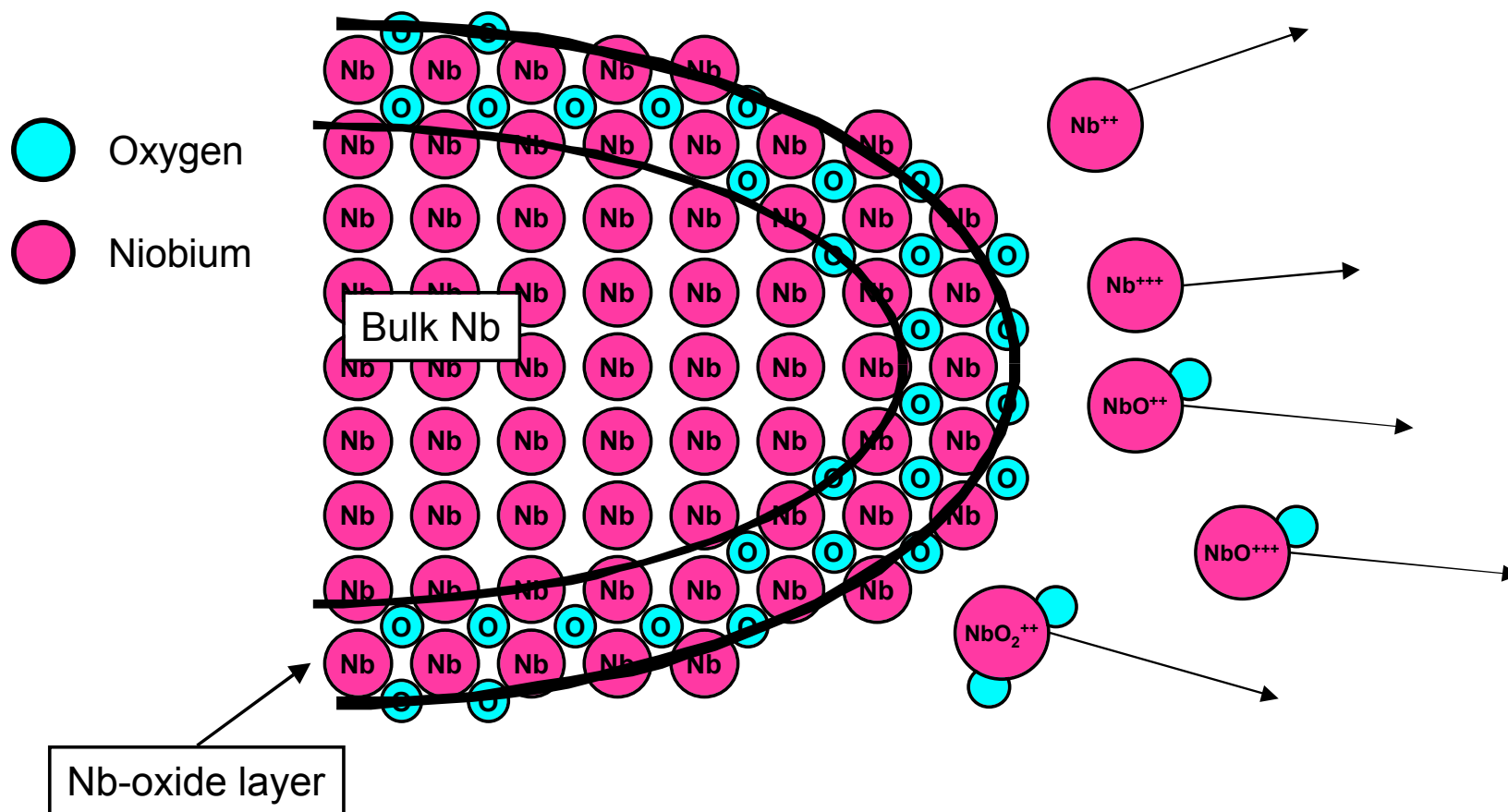


Complex mass spectrum - lots of complex ions

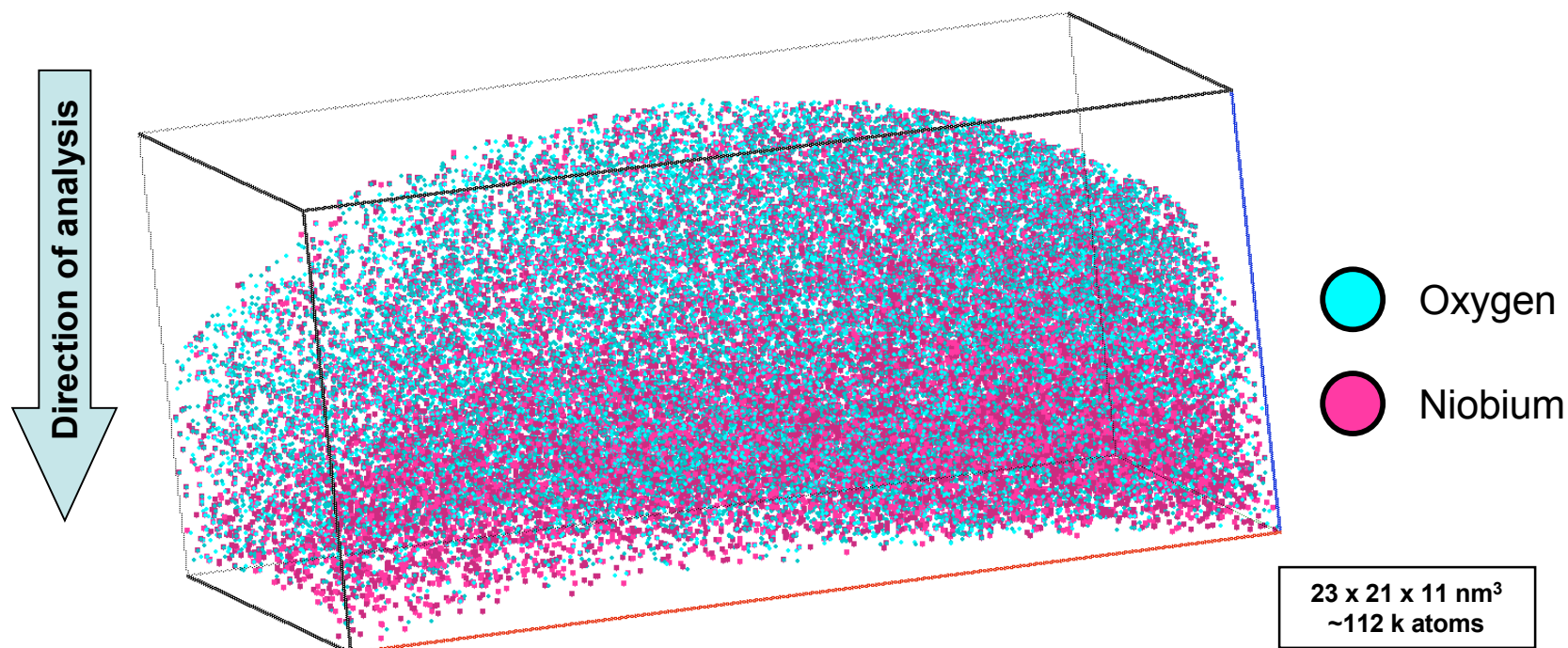


- Flight path = 128 mm
- Resolution $\approx 1/250$ (FWHM)
- T = 50K
- f = 15%
- p $\approx 8 \times 10^{-11}$ torr

Evaporation of complex ions (very schematic) - many different complex ions are field evaporated from the oxide layer of the tip

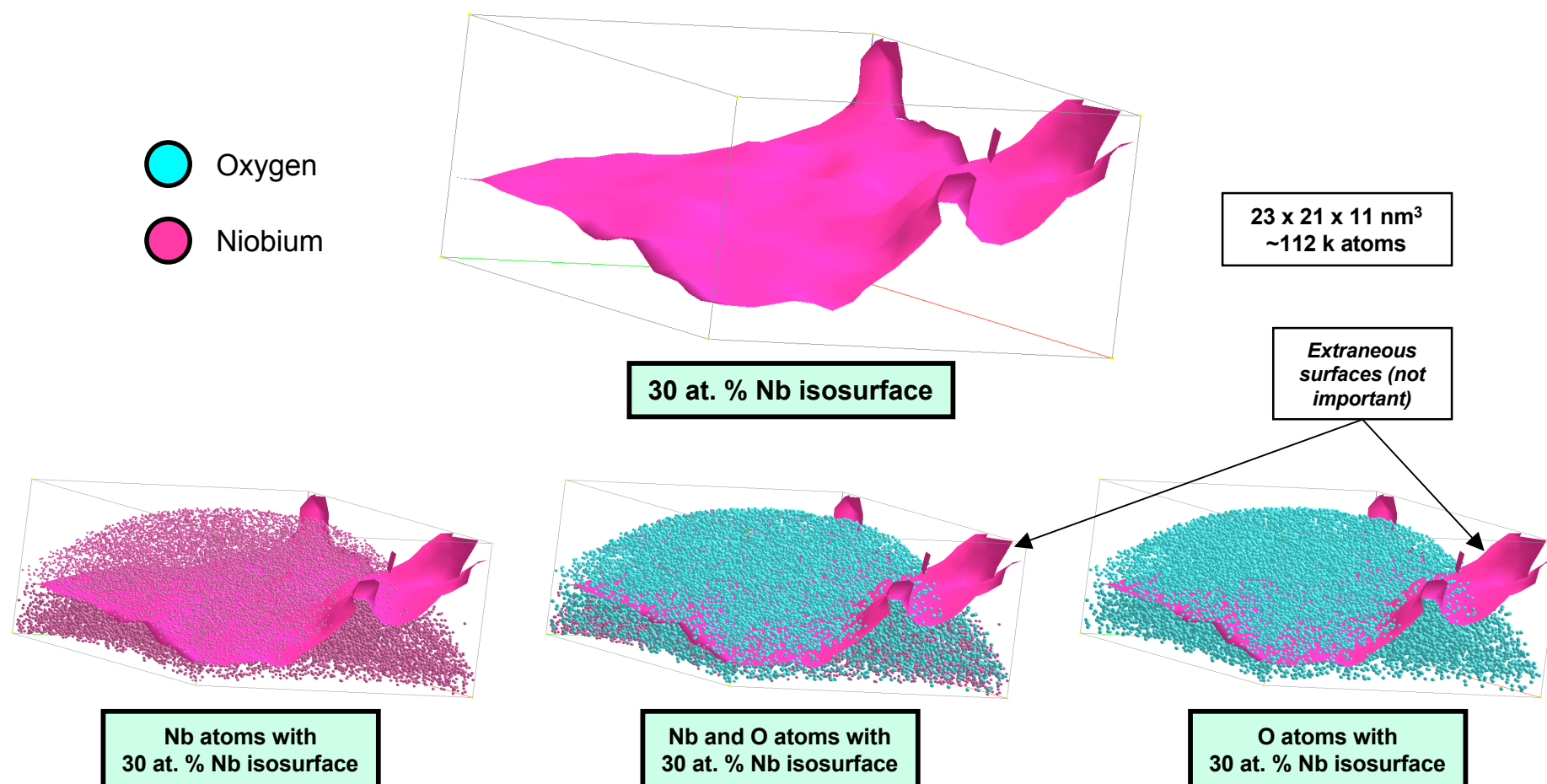


Atomic reconstruction of the transition through the oxide layer

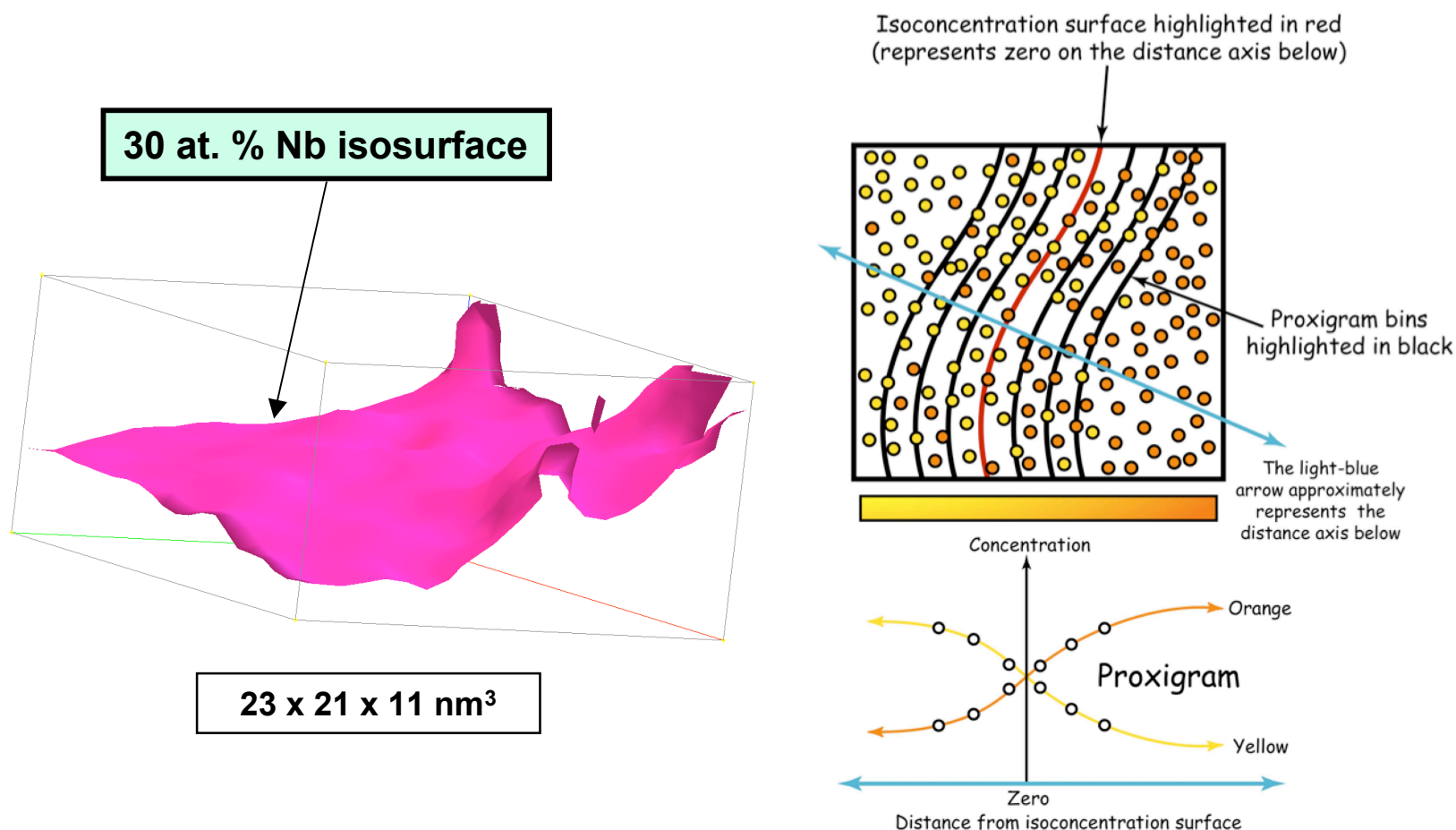


We see a clear transition from oxygen (cyan) to niobium (magenta) as we move along the analysis direction

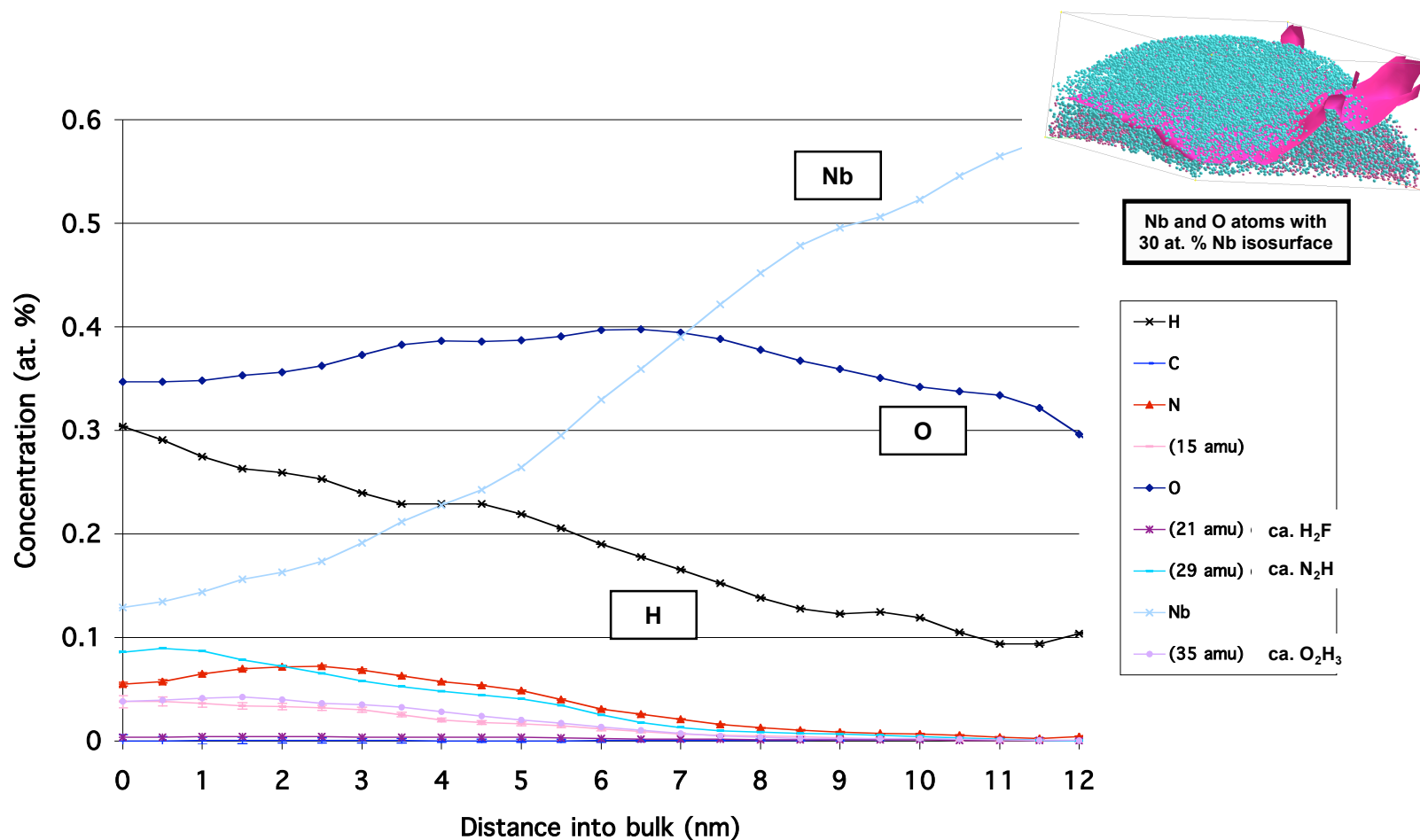
A 30 at. % Nb isosurface gives a better representation of the spatial gradients in atomic concentration



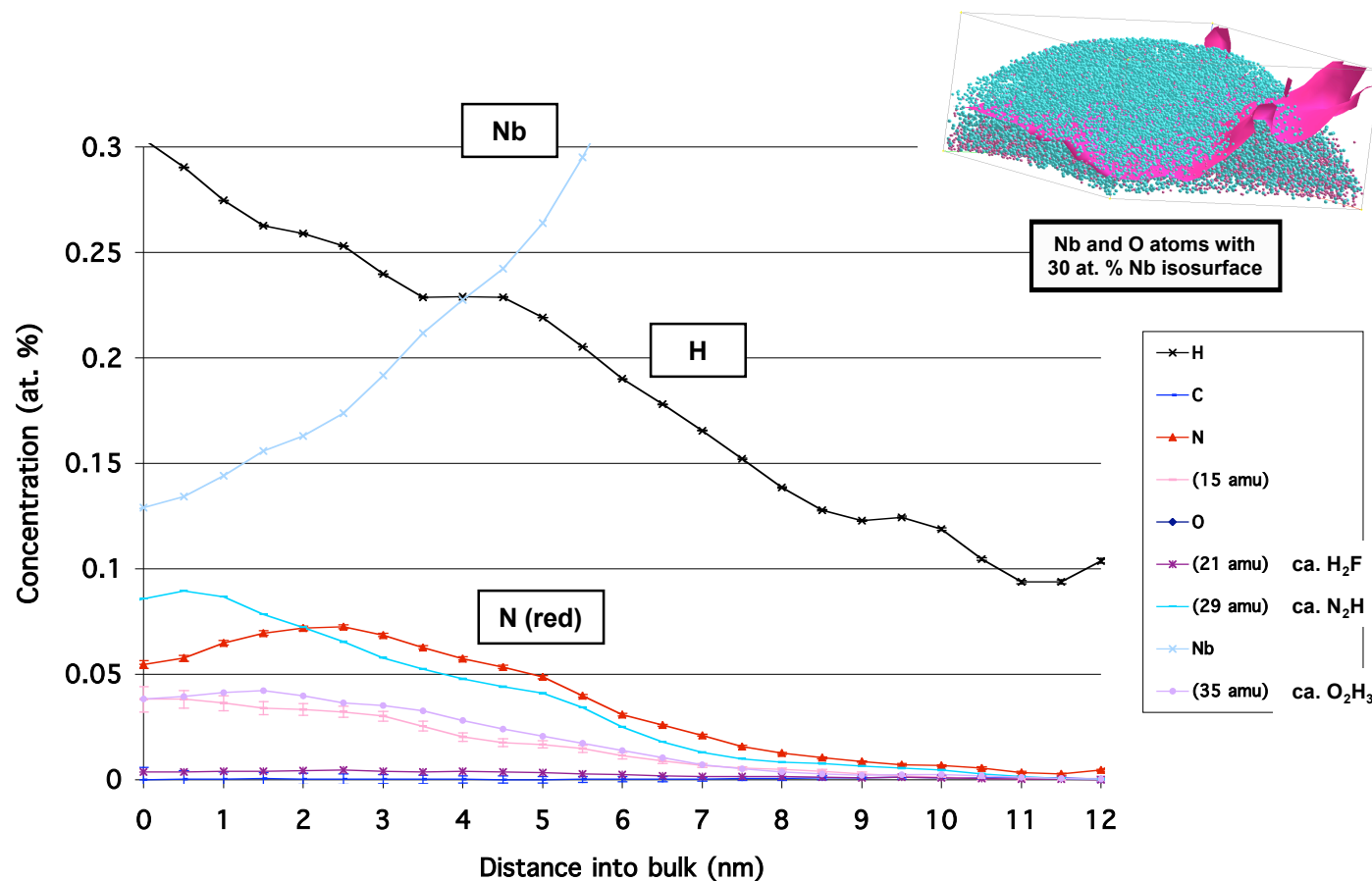
The proximity histogram (proxigram) allows for the determination of quantitative concentration profiles relative to the position of an irregularly-shaped interface



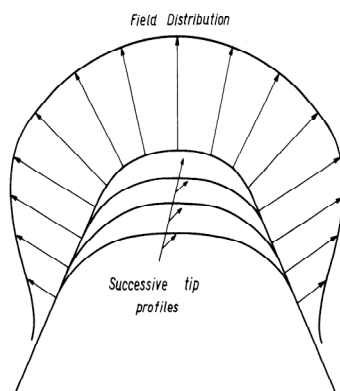
30% Nb proxigram - we see the transition from oxygen to niobium



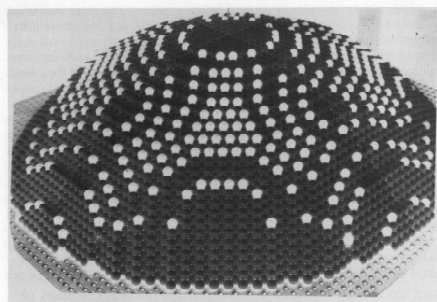
Hydrogen, residual gas atoms, and other “UFO” peaks make up nearly 50% of the ions collected



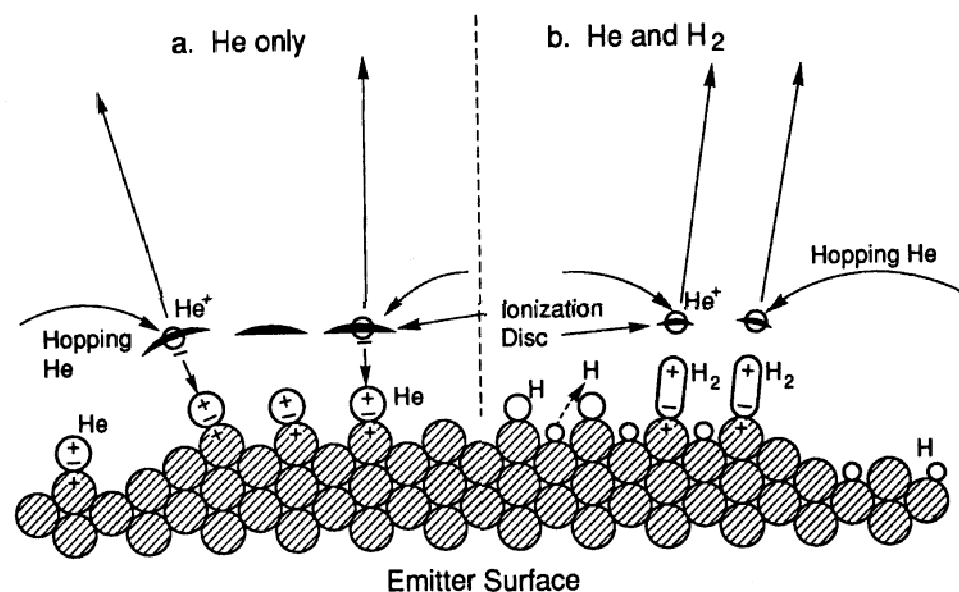
Hydrogen and residual gas atoms can come from “outside the specimen”



Electric field distribution on a atom-probe specimen (schematic)



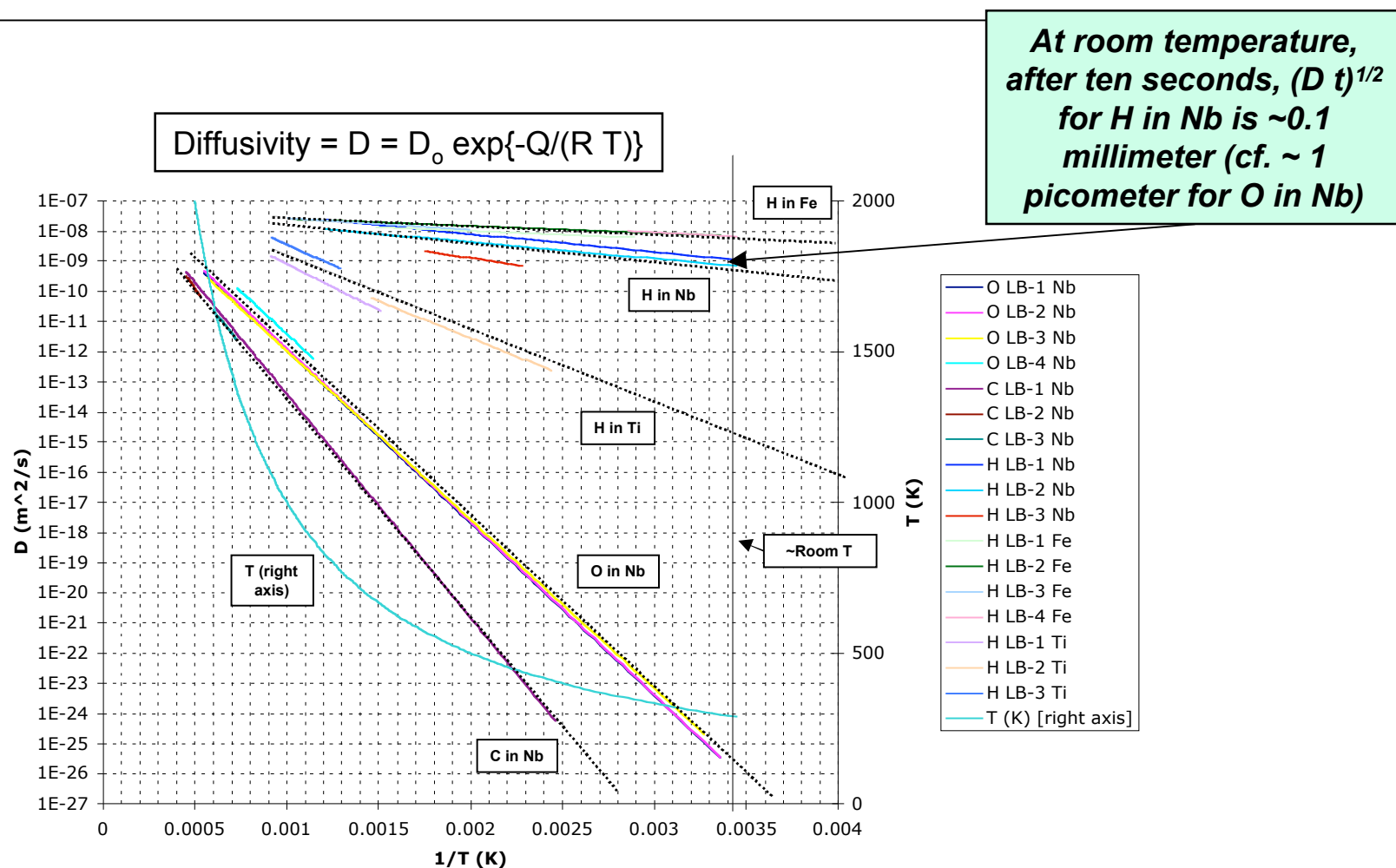
Ball model of an atom-probe tip surface (schematic)



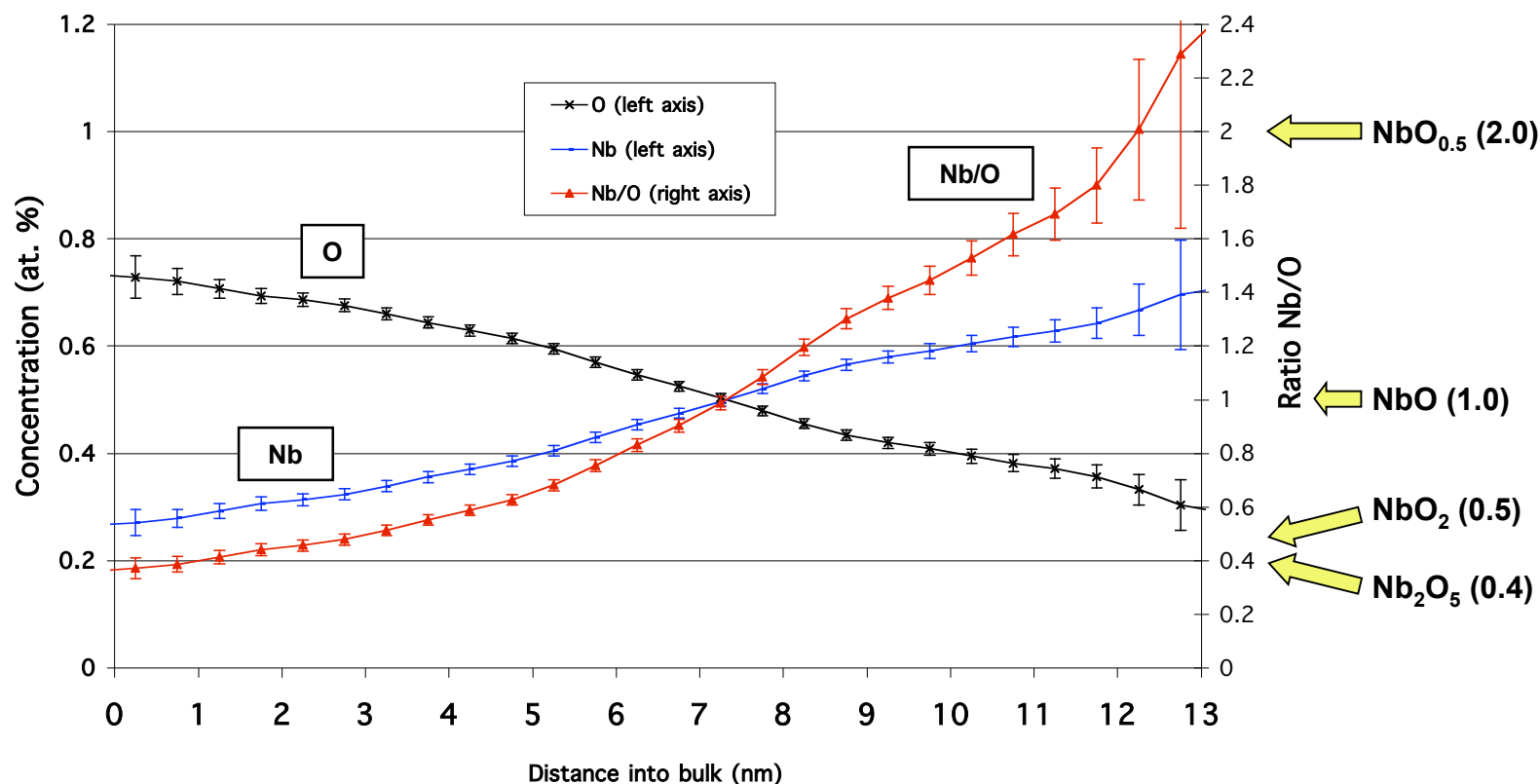
Field-ionization of gas atoms on an atom-probe tip surface

From Miller et al., (1996)

Hydrogen is extremely mobile in niobium (even at room temperature)

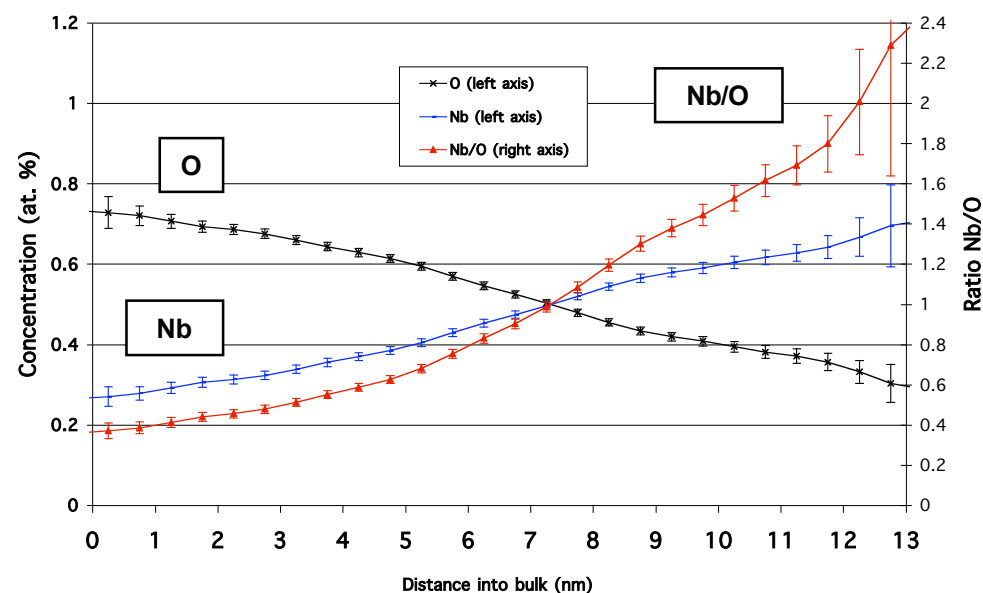
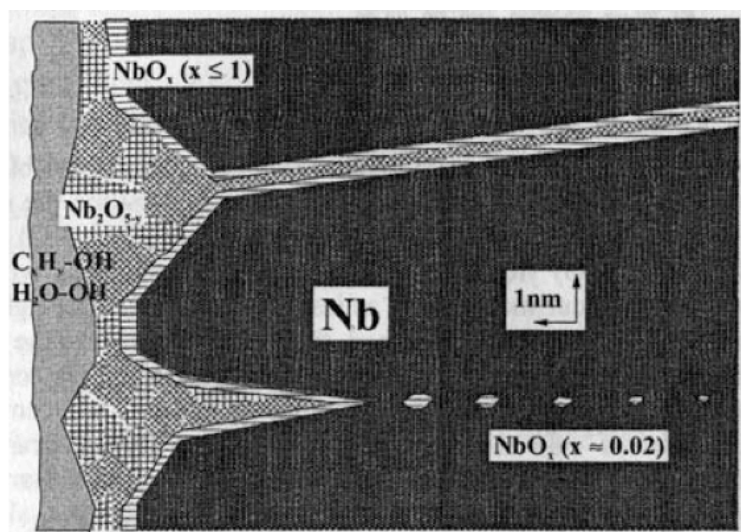


Removal of the hydrogen and residual gas atoms from the concentration gives a better picture of the transition through the oxide layer

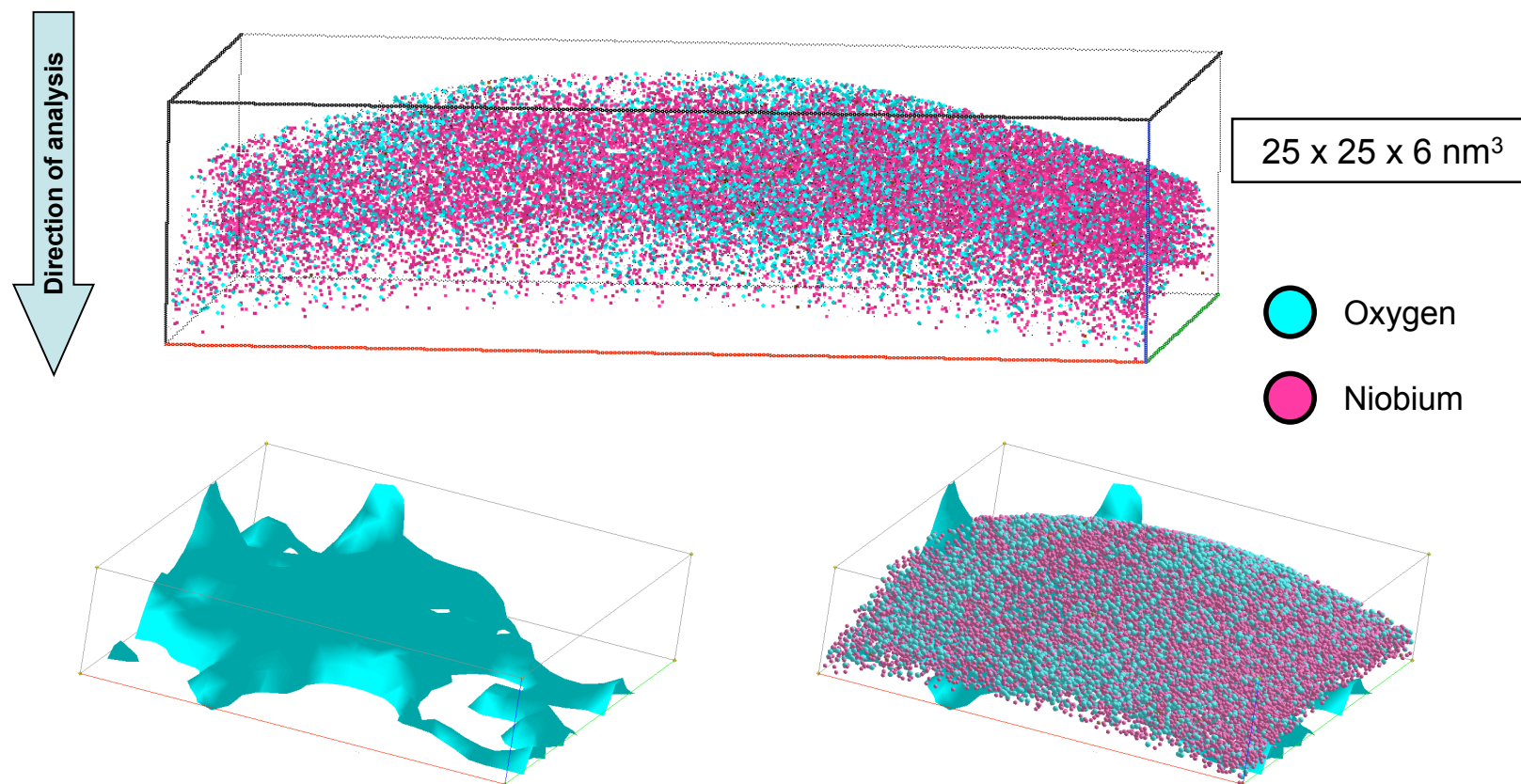


We see a clear and smooth transition from Nb₂O₅ to NbO_{0.5} (= Nb₂O)

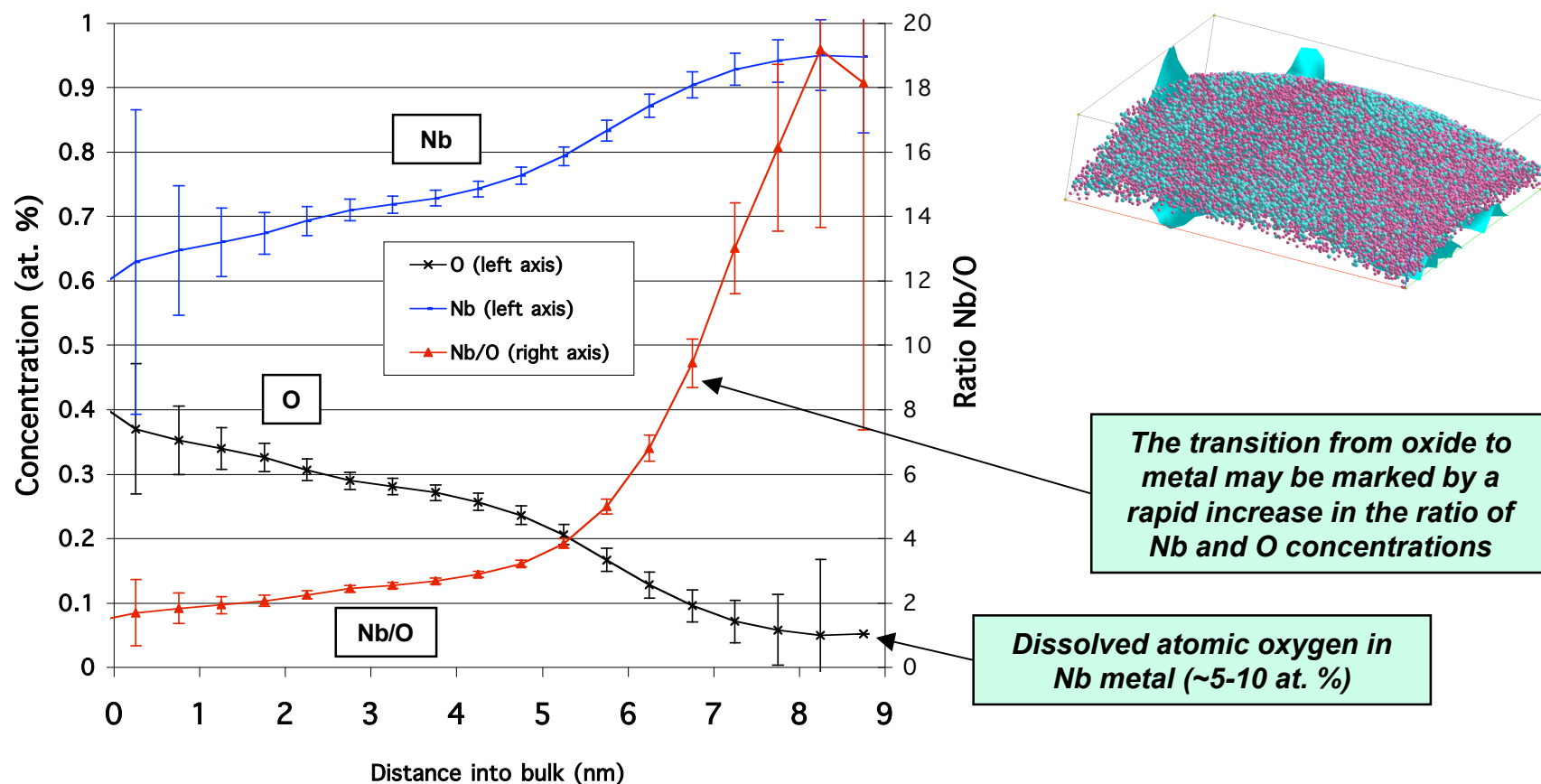
The profile corresponds, to first order, to the current models of oxide and suboxide formation on Nb



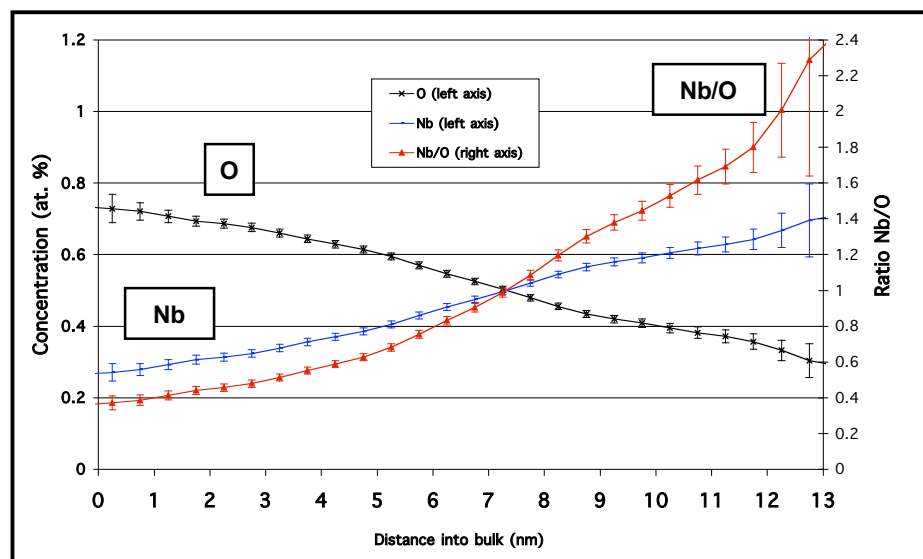
Second Nb analysis - more Nb-rich



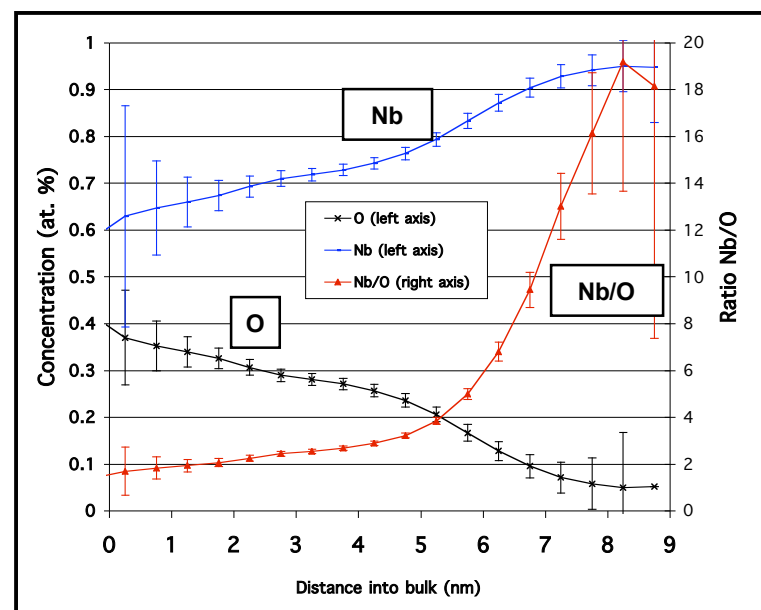
Second Nb analysis proxigram - a glimpse at the transition from oxide to Nb metal (?)



Second analysis ... a “continuation” of the first analysis

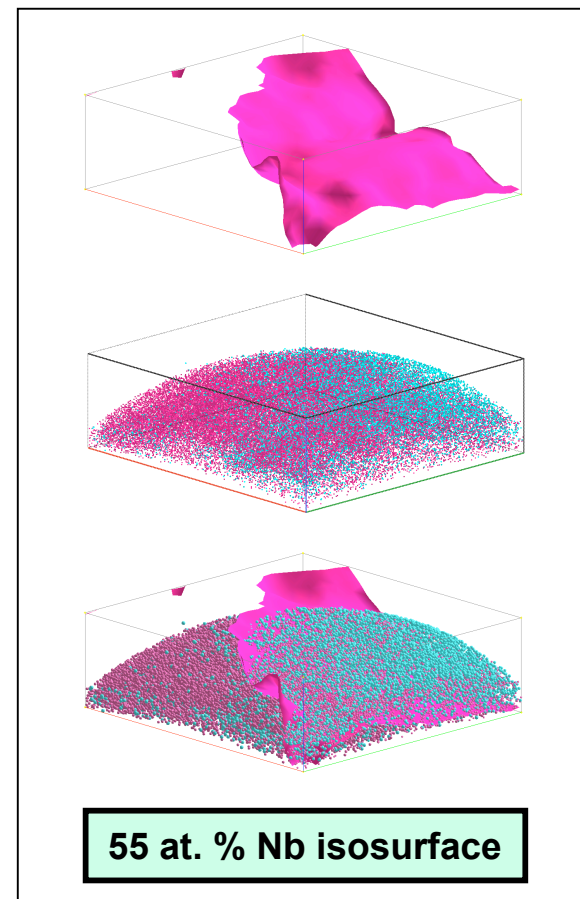
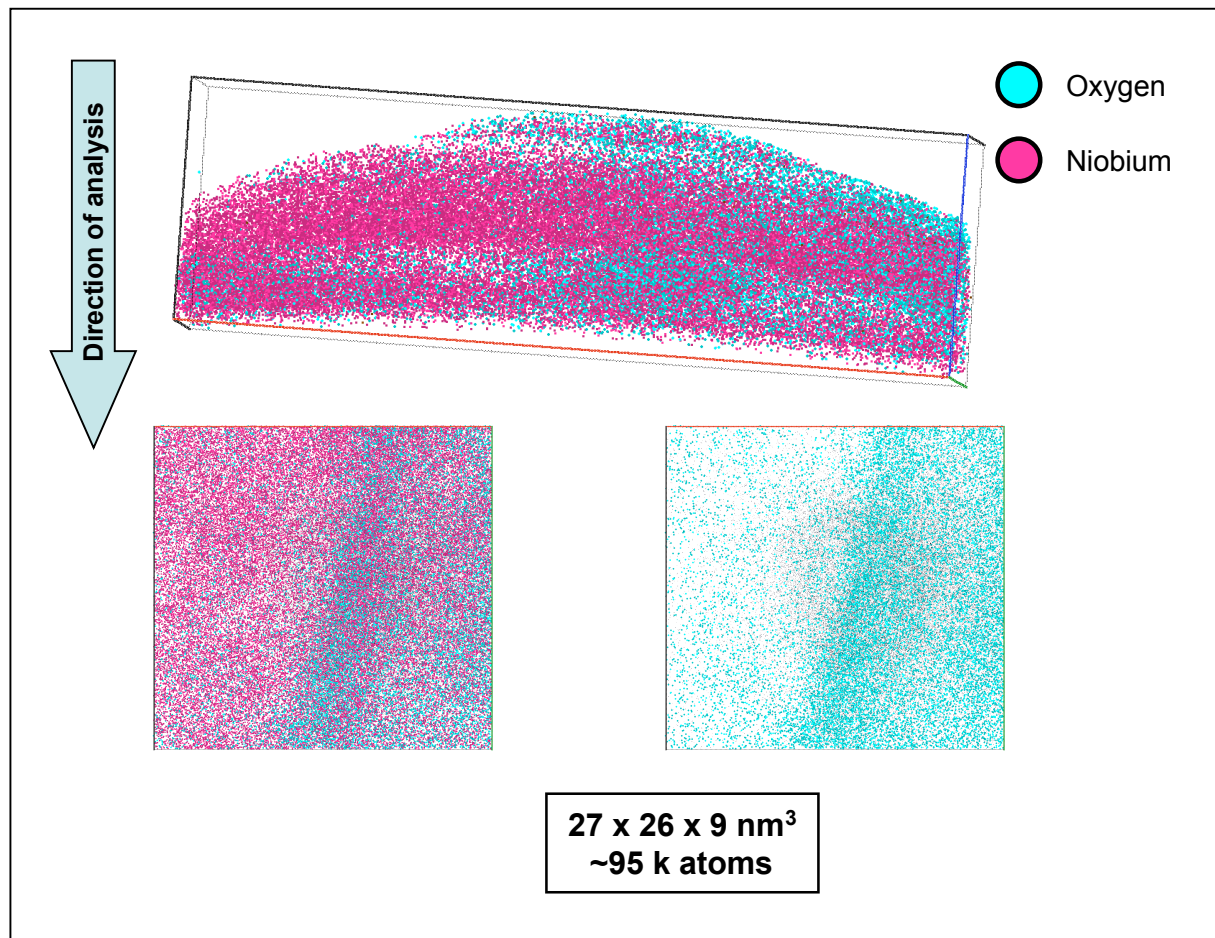


First analysis (Nb_2O_5 to Nb_2O)

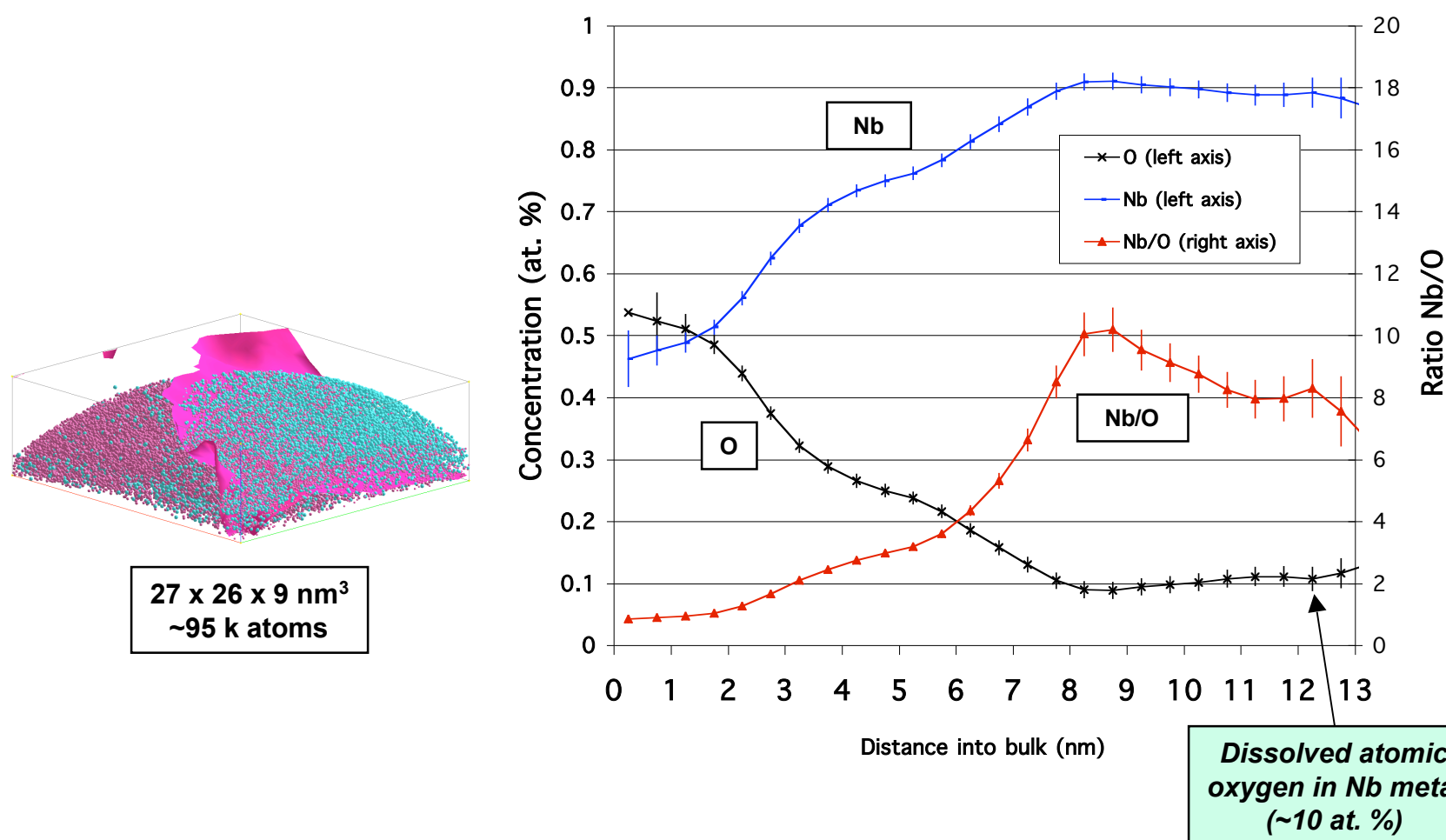


Second analysis (Nb_2O to Nb metal [?])

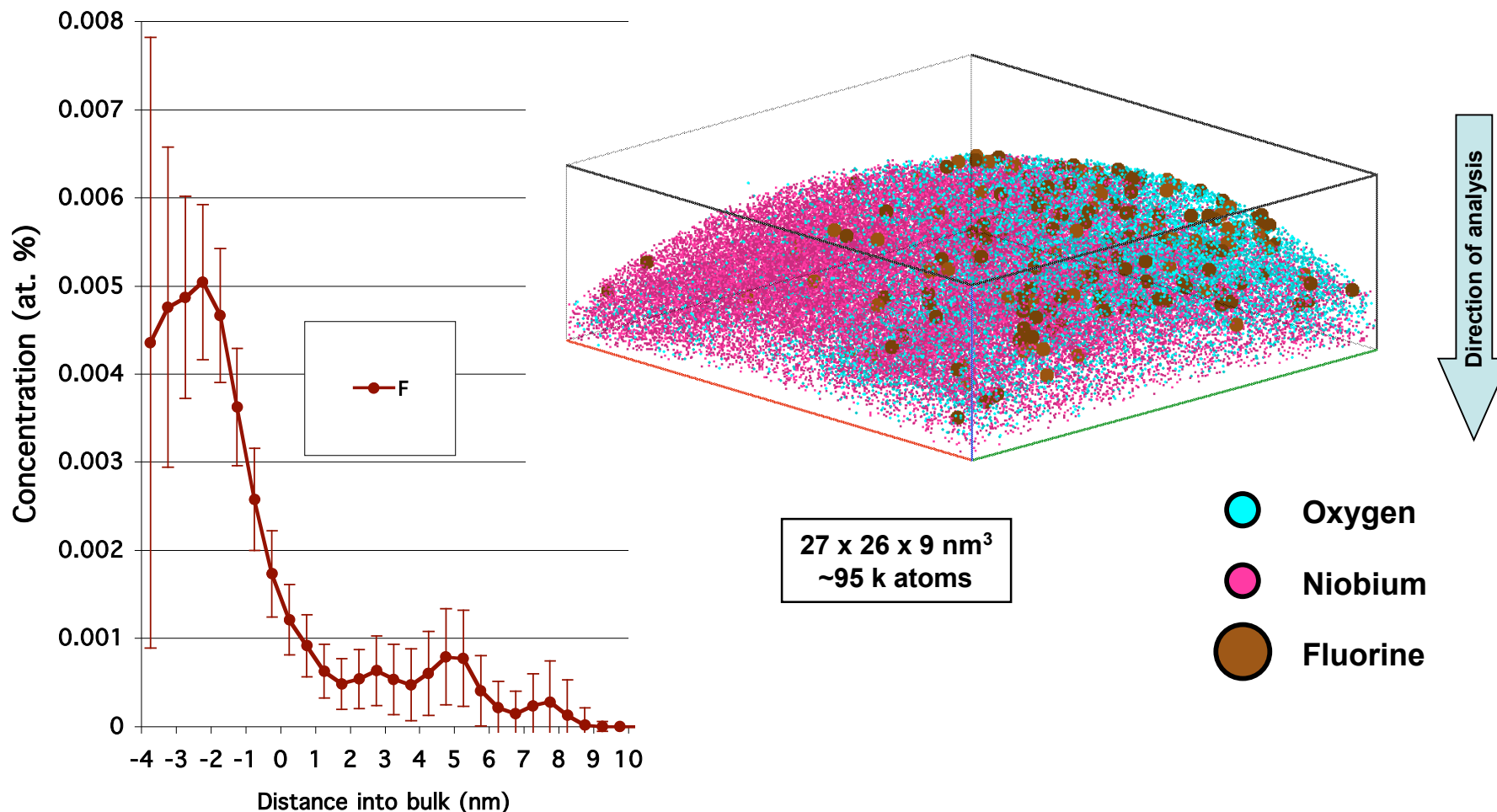
Third Nb analysis - an oxide metal interface



55% Nb isosurface and proxigram



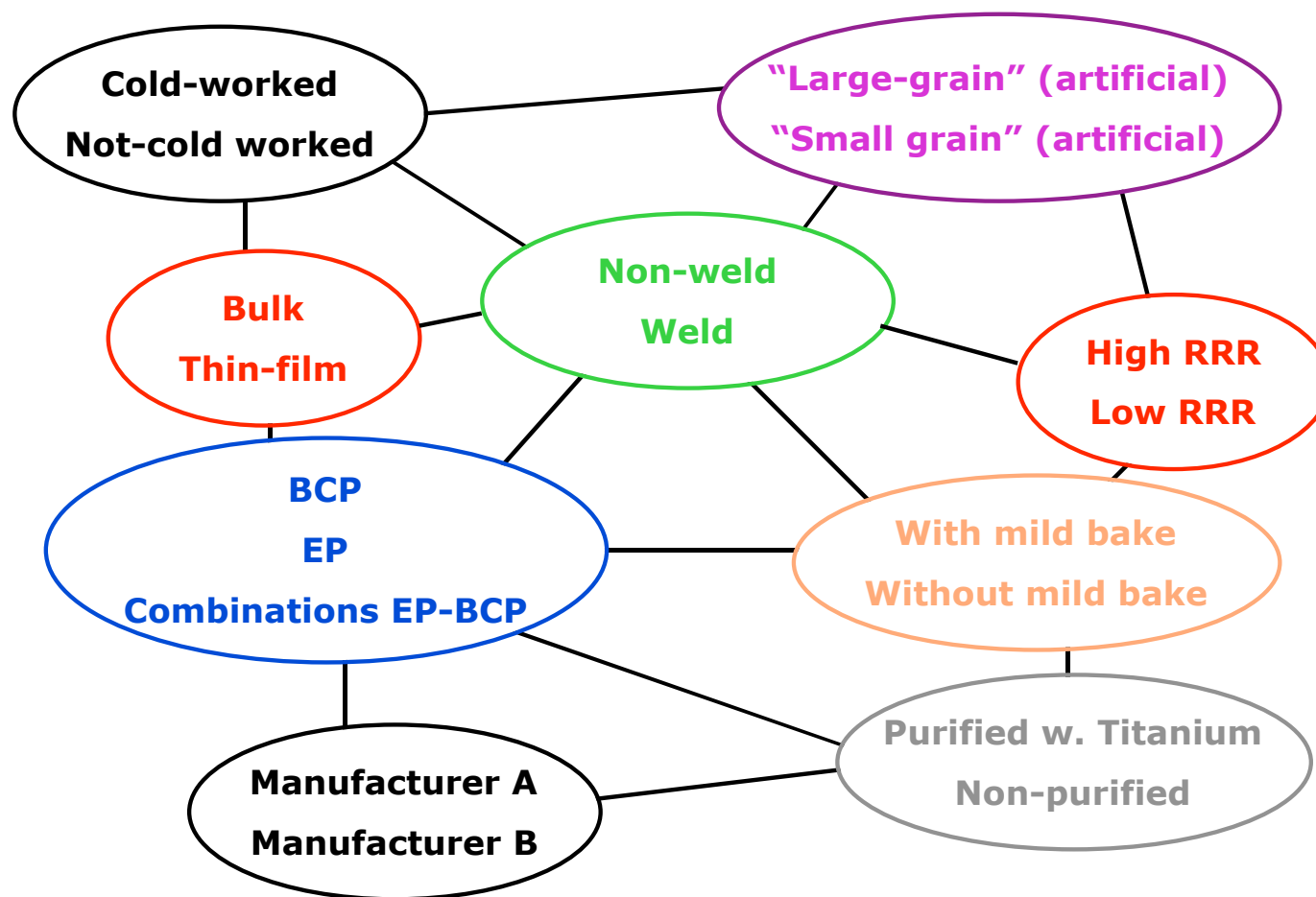
Atomic sensitivity of the technique - individual fluorine atoms on and near the surface (propensity for the oxide)



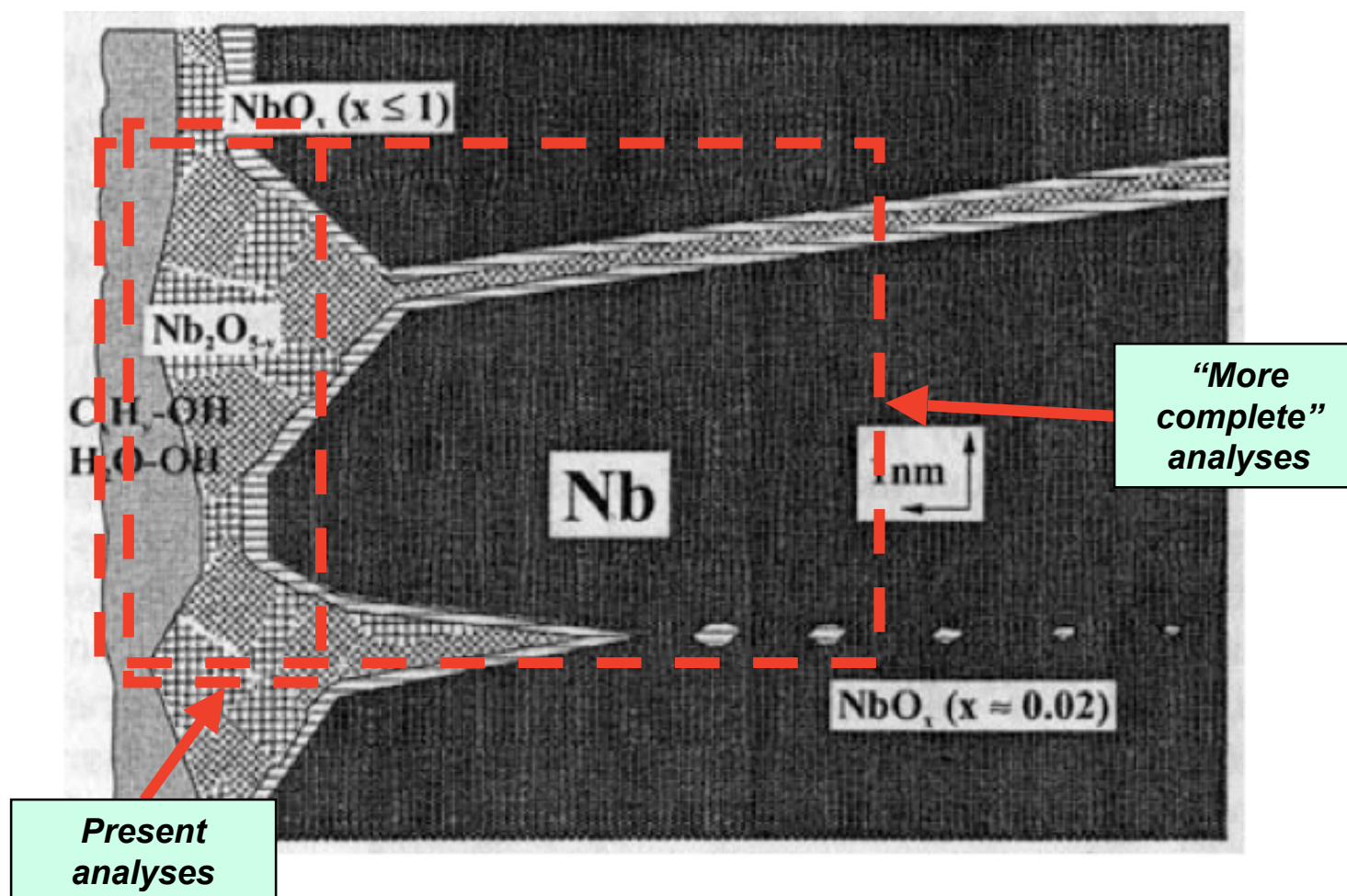
Conclusions and next steps

- Nanochemical, atomic scale analyses of the oxide surface and of the near-surface bulk niobium are being performed
 - “Smooth” transition from surface Nb_2O_5 to Nb_2O (and into the bulk Nb)
 - Ability to detect small number of contaminant atoms in the oxide surface and in the near-surface bulk niobium
 - Levels of oxygen in the near-surface bulk niobium (metal) of 5-10 at. %
- More analysis to come
 - Interpretation of mass spectra
 - Improved analysis conditions
 - Improved specimen preparation techniques (reliability and repeatability)
 - Focused ion beam (FIB) milling
 - Many classes of samples

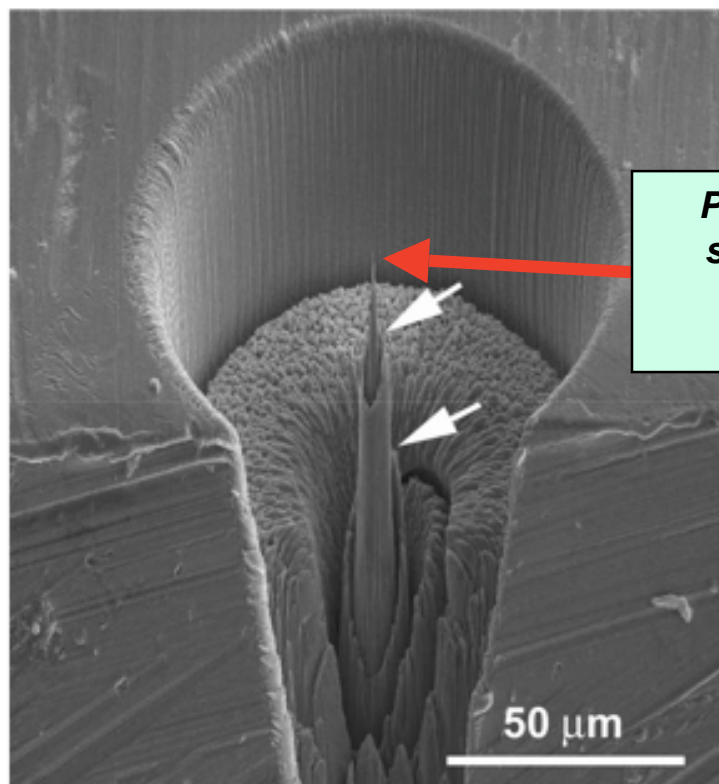
Classes of samples - effects of many, many variables on the atomic chemistry



A “more complete” run would capture much more of the atomic chemistry of the oxide surface and of the near-surface bulk niobium



Specimen preparation - focused ion beam (FIB) milling of “site-specific” LEAP specimens from niobium cavity materials



Possibility of centering a specimen on a region of interest (e.g., a grain boundary)

We will use the ANL Zeiss 1540XB dual-beam FIB to attempt “site-specific” specimen preparation

REFERENCE

Strategies for Fabricating Atom Probe Specimens with a Dual Beam FIB,
M.K. Miller, K.F. Russell and G.B. Thompson
Ultramicroscopy, 102 (2005) 287-298.